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REVERSIBLE OXYGEN ELECTRODES

REPORT NO. 4

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PURPOSE

The purpose of this program is to carry out research in order to obtain fundamental knowledge of the mechanism of adsorption of oxygen on electrode surfaces and of oxygen electrode reactions. This knowledge is essential for understanding the behavior of the oxygen electrode in hydrogen-oxygen fuel cells. Results of preliminary experiments dealing with the oxygen behavior at platinum electrodes in acid medium are presented in this report.

ABSTRACT

Adsorption of oxygen on oxide free platinum electrode has been studied in pure 1 N H_2SO_4 solutions. Coverage of electrodes with oxygen has been evaluated for various partial pressures of oxygen and temperatures. Heat of adsorption was obtained at different coverages. Dependence of rest potentials on coverage (and partial pressure) and on the temperature was determined.

In the second part of the report preliminary work on the study of oxygen electrode reactions is described.

LIST OF FIGURES

NO.	TITLE
1	Apparent coverage versus current density of "stripping".
2	Rest potential of oxide free platinum electrodes versus partial pressure of oxygen at four temperatures (right hand scale). Coverage in $\mu\text{C}/\text{cm}^2$ versus partial pressure of oxygen (left hand scale).
3	Coverage in $\mu\text{C}/\text{cm}^2$ versus rest potential at various temperatures.
4	Plot of $\log p$ versus T . p is the partial pressure of oxygen.
5	Plot of ΔH versus coverage Q .
6	Plot of $\frac{\sqrt{P}}{Q}$ versus \sqrt{p} .
7	Block diagram of the apparatus.
8	Constant current regulating circuit.
9	Furnace for thermal treatment of electrodes.
10	Anodic Tafel line.

ADSORPTION OF OXYGEN ON OXIDE FREE

PLATINUM ELECTRODES

1. Position at the end of last period of the work

In the Third Quarterly Report, the work on the adsorption of oxygen on the platinum electrode dipped into 1 N sulfuric acid solution under various partial pressures of oxygen was described and the results were discussed. In brief, the rest potential of an oxide free platinum electrode at 1 atm. oxygen partial pressure was found to be 0.98 V. The potential decreased with decreasing partial pressure of oxygen. The oxygen coverage on the electrode was determined by following on an oscilloscope the change of the electrode potential with time when a constant cathodic current was applied across the electrode. The current was sufficiently large to overcome adsorption of oxygen during this cathodic "stripping". On the oscillographs definite breaks in the potential time curves occurred at about 0.3 V with respect to the normal hydrogen electrode, and this point was taken as the end of the reduction of adsorbed oxygen. From these oscillographs, the coverage, Q , was calculated and plotted versus the partial pressure, p . A plot $\frac{\sqrt{p}}{Q}$ vs. \sqrt{p} gave a straight line which indicated dissociative adsorption of the Langmuir type. Slope of the line gave maximum coverage $Q_{\max} = 350 \mu\text{C}/\text{cm}^2$, which indicated full coverage were the adsorbed oxygen in the form Pt--OH . It was also concluded that the rest potentials are dipole potentials.

2. The aim of the work for this period.

In view of the importance of the results in evaluating the character of metal oxygen bonds and their energy, it was decided to check already obtained results and to reexamine techniques for determination of the adsorption. Also, since previous work was done at room temperature only, it was decided to extend the work to other temperatures and thus to obtain the heat of adsorption.

3. The work carried out during this period.

a. Preparation and treatment of electrodes.

Platinum electrodes in the form of wire ($d \approx 0.5$ mm) were first spot welded to a thin (0.03 mm) platinum foil. To the other end of the foil (1×4 mm² in size) a thinner ($d \approx 0.1$ mm) platinum wire, which served for contact, was also spot welded. Foil and one part of the electrode were then sealed into a ground glass tubing. This sealing proved to be better than the ordinary seal of platinum wire to the glass and prevented possible contamination of solution by leakage through the seal.

It was observed that oxygen coverage per apparent area for a given potential (and thus partial pressure) varies with pretreatment of the electrodes. An electrode cleaned by chromic acid, conc. HCl, conc. HNO₃, and afterwards washed by conductivity water gave constant values of the coverage in successive cathodic pulses. Reproducibility between the electrodes was not, however, satisfactory. Electrodes which were, after chemical treatment, polarized first anodically and then cathodically

(c.d. $\sim 50 \text{ mA/cm}^2$ for 1 sec.), gave a coverage which first decreased in successive cathodic stripping, but then, after 5 to 7 pulses had been applied, gave constant values for the coverage with a fair agreement between electrodes. Usually the apparent coverage on such electrodes was higher than on electrodes which were chemically treated only. It was also observed that the capacity of the electrodes changed with pretreatment of the electrodes. The ratio between the capacity and the coverage, however, was the same independent of the treatment of the electrodes. Differences in coverage for the same rest potentials were thus ascribed to the changes in the area of the electrodes which were differently treated.

The roughness factor was calculated from double layer capacity measurements using the d.c. transient techniques. The d.c. transients were recorded at $10 \mu \text{ sec}$ and in the 10 mV range on an oscilloscope. From the formula

$$i = C_{\text{D.L.}} \left(\frac{dV}{dt} \right)_{t=0}$$

the capacity was calculated as $27 \mu\text{F/cm}^2$ for electrodes anodically and cathodically treated (or as $18\text{--}20 \mu\text{F/cm}^2$ for chemically treated electrodes). Since the low capacity values obviously indicate the absence of any specific adsorption of ions, the roughness factor was obtained by dividing the observed value of capacity with $16 \mu\text{F/cm}^2$. The latter value is the capacity at a mercury-sulfuric acid solution interface at the electrocapillary maximum. Thus the roughness factor of anodically and then cathodically treated electrodes was about 1.7. In the coverage-potential measurements, anodically and cathodically treated electrodes were used and the coverage was corrected for the corresponding roughness factor.

b. Determination of the limiting currents for galvanostatic transients.

During the cathodic stripping, if the cathodic current is small, additional oxygen from the solution may diffuse to the electrode and become adsorbed before the process of stripping is completed. This would affect measured values of coverage. Above a certain current density, there is no change in apparent coverage, meaning that the amount of additionally adsorbed oxygen is negligible. Apparent coverage versus current density was plotted for 20°C and 80°C (fig. 1). At 20°C, additional adsorption of oxygen above about 10 mA/cm² was negligible, and at 80°C, it was negligible above about 20 mA/cm². In all experiments 50 mA/cm² was chosen for cathodic stripping.

c. Adjustment of the oxygen partial pressure and equilibration of solution.

The partial pressures of oxygen were adjusted by flow meters from 0.005 to 1 atm. Mixtures of oxygen and nitrogen were bubbled through the solution. Accuracy of the adjustment of the oxygen partial pressure was checked by polarographic analysis. Precision of the adjustment by flow meters was within 5% of partial pressure of oxygen. It was also concluded from the polarographic analyses that equilibration of the solution in our experimental set-up occurs in less than two minutes when the oxygen partial pressure is changed. In all measurements of coverage, the adjusted mixture of gases was bubbled for five minutes. During the measurements themselves, gas was not bubbled.

Values of the adjusted partial pressures of oxygen were corrected for water vapor pressure above the solution. This correction was appreciable at temperatures above the room temperature.

d. Cell and the solution.

For measurements of adsorption at various temperatures a new cell was designed and made. The main compartment of the cell was jacketed so that thermostated water could be circulated. Hydrogen reference electrode and counter electrode compartments were separated from the main compartment by stop-cocks (see Report No. 1). Normal H_2SO_4 solution prepared with conductivity water was kept at various constant temperatures to within $\pm 0.5^\circ\text{C}$.

e. Experimental Results.

The following measurements were taken:

(i) Rest potentials (against hydrogen electrode in the same solution) at various partial pressures and temperatures (fig. 2).

(ii) Coverage (in $\mu\text{C}/\text{cm}^2$) at various rest potentials and temperatures (fig. 3).

At one atmosphere pressure of oxygen and at 0°C the rest potential reached the value* of 1.005 ± 0.005 V. Coverage at a given potential appeared to be independent of temperature (at least in the temperature range of these experiments - from 0°C to 80°C). To a first approximation, the coverage-potential relationship was linear, deviating, however, at low partial pressures. In figure 4, the coverage-partial pressure isotherms are plotted for four temperatures.

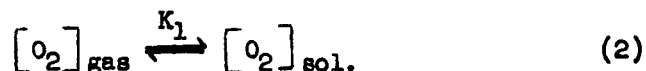
*Somewhat higher value of the potential than previously reported - Report No. 3 - is due to higher purity of the solution.

f. Discussion of the results.

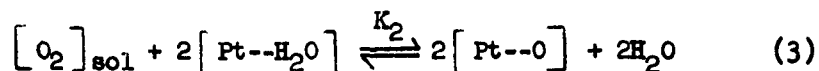
It can be shown that the Clausius-Clapeyron equation

$$\left[\frac{d \ln K}{dT} \right]_V = - \frac{\Delta E}{RT^2}, \quad (1)$$

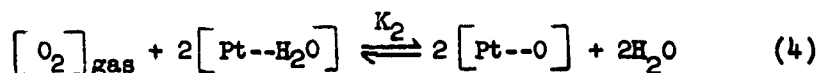
where K is equilibrium constant and ΔE the enthalpy of the reaction, is applicable to adsorption from solution when the volume, V , is replaced by the coverage. The equilibrium constant can be obtained as follows. Oxygen in the solution is in equilibrium with the dissolved oxygen:



With the assumption that oxygen has to remove already adsorbed water molecules in order to become adsorbed, it follows:



By adding (2) and (3) one obtains:



and

$$K = \frac{[Pt--O]^2}{[O_2]_{\text{gas}} [Pt--H_2O]^2}. \quad (5)$$

Regardless of the assumption made about the adsorption, i.e., is it dissociative or not - which would change exponents in concentrations, and, also, regardless in what units $[Pt--O]$ and $[Pt--H_2O]$ are expressed - as long as the exponents of both are the same, for the same coverage, the equilibrium constant K is inversely proportional to oxygen partial

pressure, p . With this, equation (1) and (5) give:

$$\left[\frac{d \ln p}{dT} \right]_Q = \frac{\Delta E}{RT^2} \quad (6)$$

Plots of $\log p$ versus T for various constant coverages is given in figure 4. From the slopes at 0°C , ΔE was evaluated for various coverages (fig. 5). It changes with coverage; at $40 \mu\text{C}/\text{cm}^2$ it is 9,600 cal/mol O_2 and at $90 \mu\text{C}/\text{cm}^2$, 2300 cal/mol O_2 . The heat of adsorption will be discussed further below.

Since $[\text{Pt}-\text{O}]$ in equation (5) is proportional to the coverage, and with the assumption that each oxygen atom replaces one molecule of water on the electrode, equation (5) can be written in the form:

$$(pK)^{1/2} = \frac{aQ}{1 - aQ}, \quad (7)$$

or:

$$Q = \frac{1}{a \left[1 + (pK)^{-1/2} \right]}. \quad (7a)$$

Maximum value of the coverage, Q_{max} , when the pressure is sufficiently large, is equal to $1/a$. Equation (7) can be transformed into:

$$\frac{\sqrt{p}}{Q} = a \left(\sqrt{p} + \sqrt{\frac{1}{K}} \right).$$

Plot of $\frac{\sqrt{p}}{Q}$ versus \sqrt{p} (fig. 6) gives at higher values of the pressure a straight line with the slope $a = 7.37 \cdot 10^{-3} \frac{\text{cm}^2}{\mu\text{C}}$. At low values of the pressure, the lines deviate as may be expected since K is not independent of coverage. K is proportional to $\exp(-\frac{\Delta E}{RT})$, and ΔE changes with the coverage. At higher partial pressures, the coverage changes little with pressure and $\sqrt{1/K}$ can be considered constant. With this, the maximum coverage is $135 \frac{\mu\text{C}}{\text{cm}^2}$ which corresponds approximately to one oxygen to four

platinum atoms. Similar straightening of the line at higher pressures does not occur when p/Q is plotted against p . This indicates that the adsorption is dissociative.

The heat of adsorption, as obtained in these experiments, does not include the heat of dissociation of oxygen. Heat of adsorption of oxygen atoms will be by 117 kcal/mol O_2 greater, or approximately 125 kcal/mol. The high value of reaction means that oxygen is chemisorbed on the platinum electrode.

The variation of rest potential with partial pressure of oxygen does not follow the Nernst relationship, and hence, it is not a thermodynamic phase boundary potential. The potential-coverage relationship over a wide range of coverage may be considered as linear, indicating that the potentials are dipole potentials and that the electrodes behave as perfectly polarizable electrodes.

4. Short term aim of the work.

It is planned to complete analysis of the experimental results, in particular, it is intended to explain the variation of heat of adsorption with coverage taking into account interaction forces between adsorbed species on the electrode. Experiments with other transition metals will be carried out shortly. These experiments will serve to further elucidate the nature of the metal-oxygen bond, and the role of the d-character of transition metals on the heat of adsorption and the maximum coverage by oxygen.

MECHANISM OF OXYGEN ELECTRODE REACTIONS

1. Aim of the work.

The aim of the work is to study the oxygen electrode reactions. Following previous work in this Laboratory on the mechanism of oxygen evolution reaction and on the reversible oxygen potential on platinum electrodes, a new project on reversible oxygen electrodes and oxygen electrode reactions was designed. It is intended to identify the rate determining step in the mechanism of oxygen electrode reactions on various metals. In particular it is intended to examine the nature of oxides formed on electrodes and their effect on the mechanism of oxygen reactions. Work on this project was commenced during October 1962.

2. Experimental set-up.

During this report period an apparatus was set up. The apparatus is similar to that described in the Report No. 1. It consists of an all glass cell with three compartments - one for the test electrode, one for the reference electrode, and one for the counter electrode. The electrical circuit is arranged so that any desired current can be passed through the test electrode while measuring the potential continuously on a recorder. A potentiometer is used to measure the steady state values more accurately. The arrangement is shown in fig. 7. The constant current regulating circuit is given in figure 8. It consists of two micropots in series to drop the potential of a 90 volt dry battery and a switch to choose an appropriate series resistance.

3. Experimental results

The initial trials to obtain reversible oxygen potential were made in anodically pre-electrolyzed 0.1 N/H₂SO₄ solution. Electrodes which were initially anodized with 10⁻³ A/cm² for 20 minutes and then kept in oxygen atmosphere above the solution for 24 hours* did not give 1.23 V potential. The electrodes sometimes gave potential plateaus at 1.3 volts. The reproducibility was poor and the potentials usually fell to less than 1.0 volts. Some electrodes also showed a potential of about 1.4 volts.

In order to ascertain just what was causing the difficulties, it was decided to make oxygen evolution Tafel lines in the anodically pre-electrolyzed solutions. Depolarization of the electrodes occurred at about 10⁻⁶ A/cm². Anodic pre-electrolysis was discontinued and the H₂O₂ purification method** adopted. In order to standardize electrode preparation, the method of Bockris and Huq*** was used. This consists of heating the electrode to 500°C in purified O₂ for two hours, and sealing it in a glass bulb. For this purpose a special small furnace was designed (fig. 9).

After a number of trials, good Tafel lines were obtained. One is given in figure 10. Exchange current density is usually about 3·10⁻¹⁰ A/cm², and the slope is about 0.1 V. Zero current potential is always close to the reversible oxygen potential, 1.23 V, and it stays at this potential for many hours.

* N. Watanabe and M.A.V. Devanathan, to be published.

** W. Visscher and M.A.V. Devanathan, to be published.

*** J. O'M. Bockris and A.K.M.S. Huq, Proc. Roy. Soc., A237, 277 (1956).

4. Short term aim of the work.

The short term aim of the work is to examine the effect of thermal treatment of electrodes on their behavior in the same electrolyte and also to check the importance of solution purification by various methods keeping the preparation of electrodes the same. When more experimental data are collected their analysis will begin.

SUMMARY AND CONCLUSIONS

Adsorption of oxygen on oxide free platinum electrodes in pure 1 N H_2SO_4 solutions saturated with oxygen at various partial pressures has been determined for 0, 20, 50 and 80°C. Heat of adsorption has been evaluated for various coverages; it decreases with increasing coverage. At 0°C, the heat of adsorption is 9,600 and 2,300 cal/mol O_2 for 40 C/cm^2 and 90 $\mu\text{C}/\text{cm}^2$, respectively. Plot of $\sqrt{\frac{p}{Q}}$ versus \sqrt{p} indicates that adsorption is disassociative. Maximum value of the coverage is about 135 $\mu\text{C}/\text{cm}^2$, corresponding to one oxygen atom to four platinum atoms.

Good tafel lines have been obtained in oxygen evolution reaction. Zero current potential corresponds to reversible oxygen potential, 1.23 V.

IDENTIFICATION OF KEY PERSONNEL

The following personnel performed the approximate number of man-hours of work shown in the fourth quarter on this project.

John O'M. Bockris

Estimated 33 man hours

Project Director with academic background in physical electro-chemistry.

B.S. in Physical Chemistry, Imperial College (London)

Ph.D. in Physical Chemistry, Imperial College (London)

D.Sc., University of London

Aleksander Damjanovic

Estimated 125 man hours

Project Supervisor with academic background in physical chemistry and physical metallurgy.

B.S. in Chemical Engineering, Belgrade University

Ph.D., Cavendish Laboratory, Cambridge University

M. L. Bhaskara Rao

560 man hours

B.Sc., University of Mysore

M.Sc., University of Rajaputana

D.Phil., University of Calcutta

Marvin Genshaw

560 man hours

B.S., Chemistry, Michigan College of Mining and Technology.

Technicians

Charles Searles

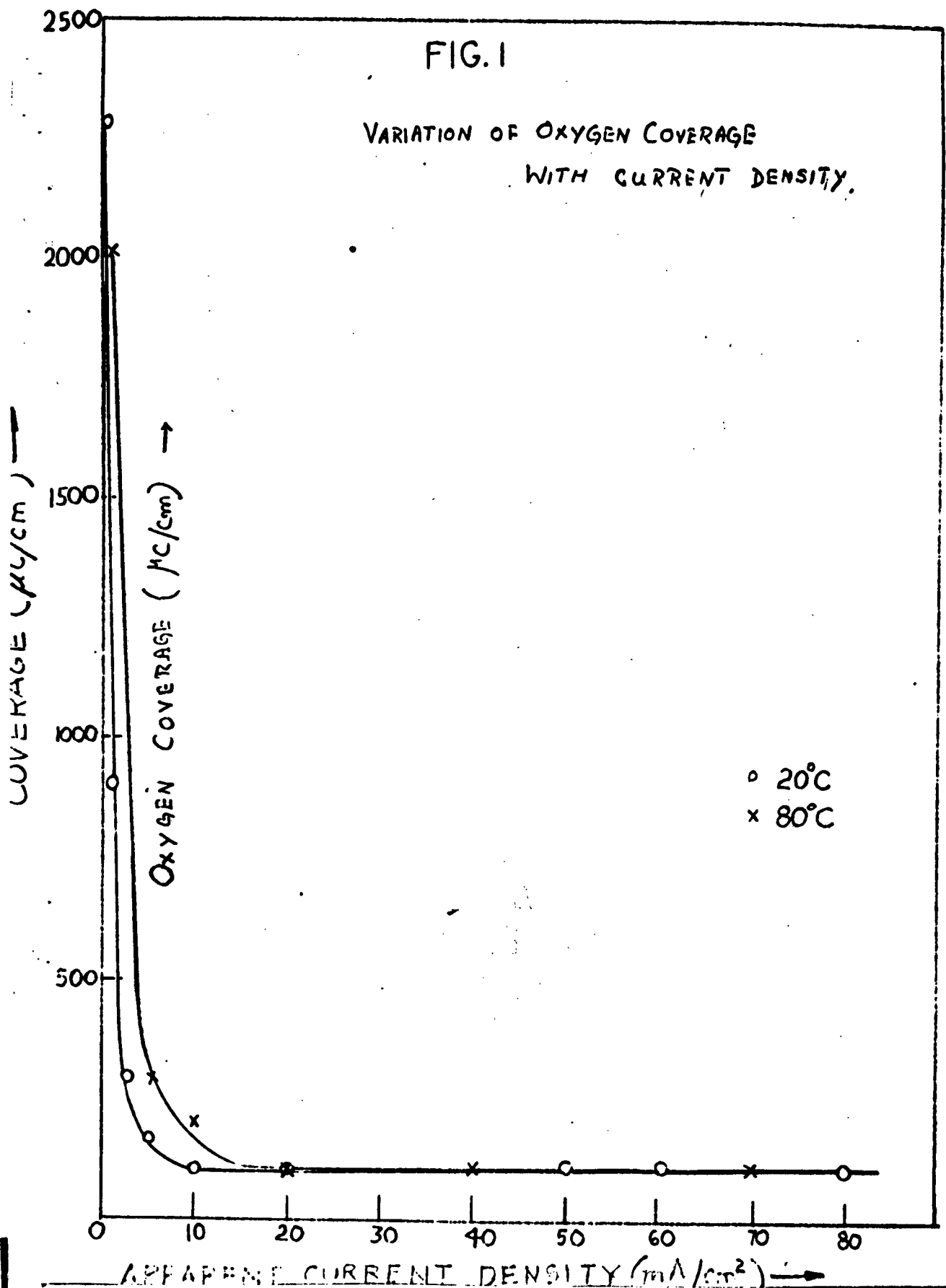
Georg Myers

Alan Saunders

┌
 - Total 30 man hours
 └

FIG. 1

VARIATION OF OXYGEN COVERAGE
WITH CURRENT DENSITY.



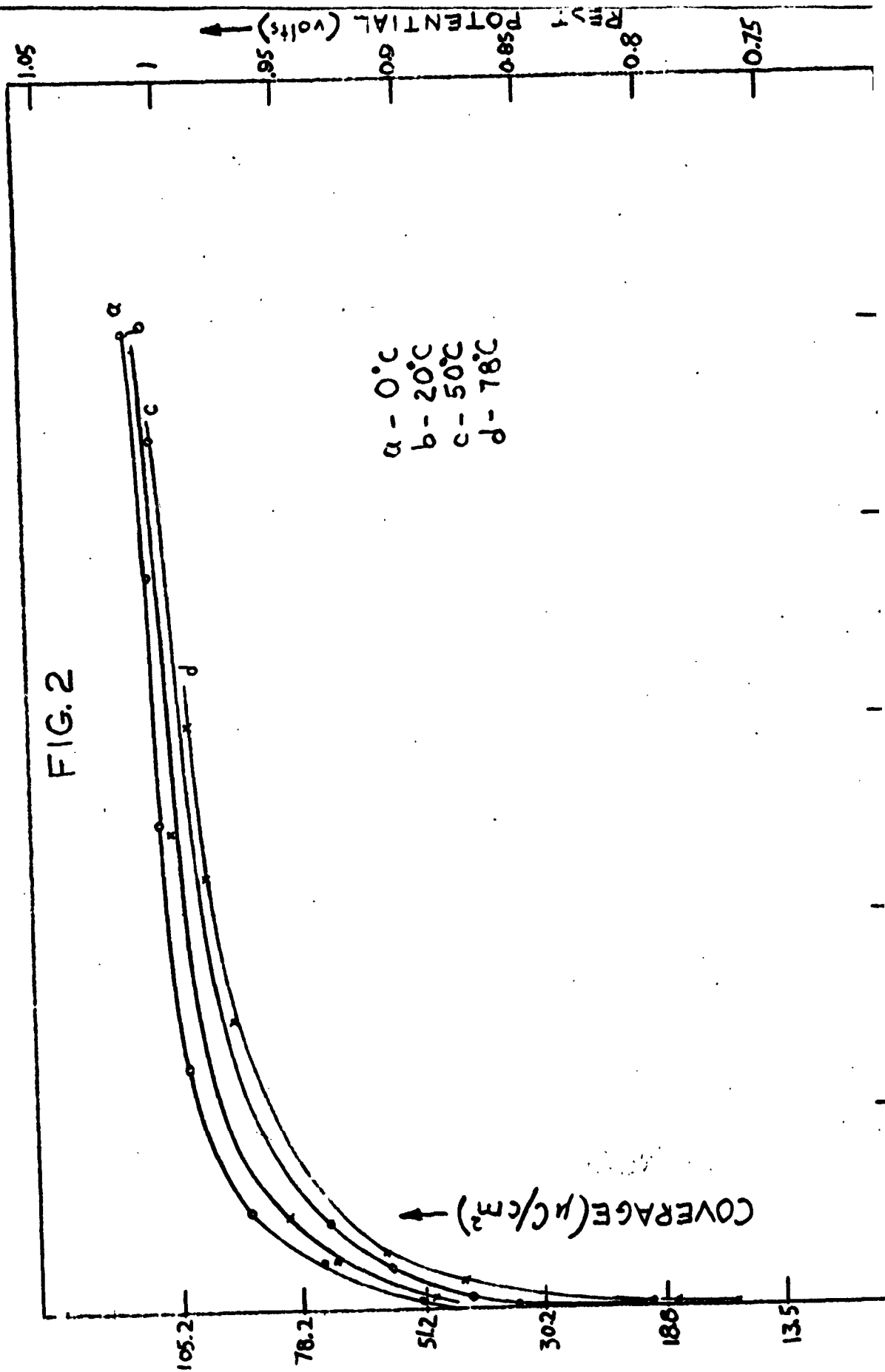


FIG. 3

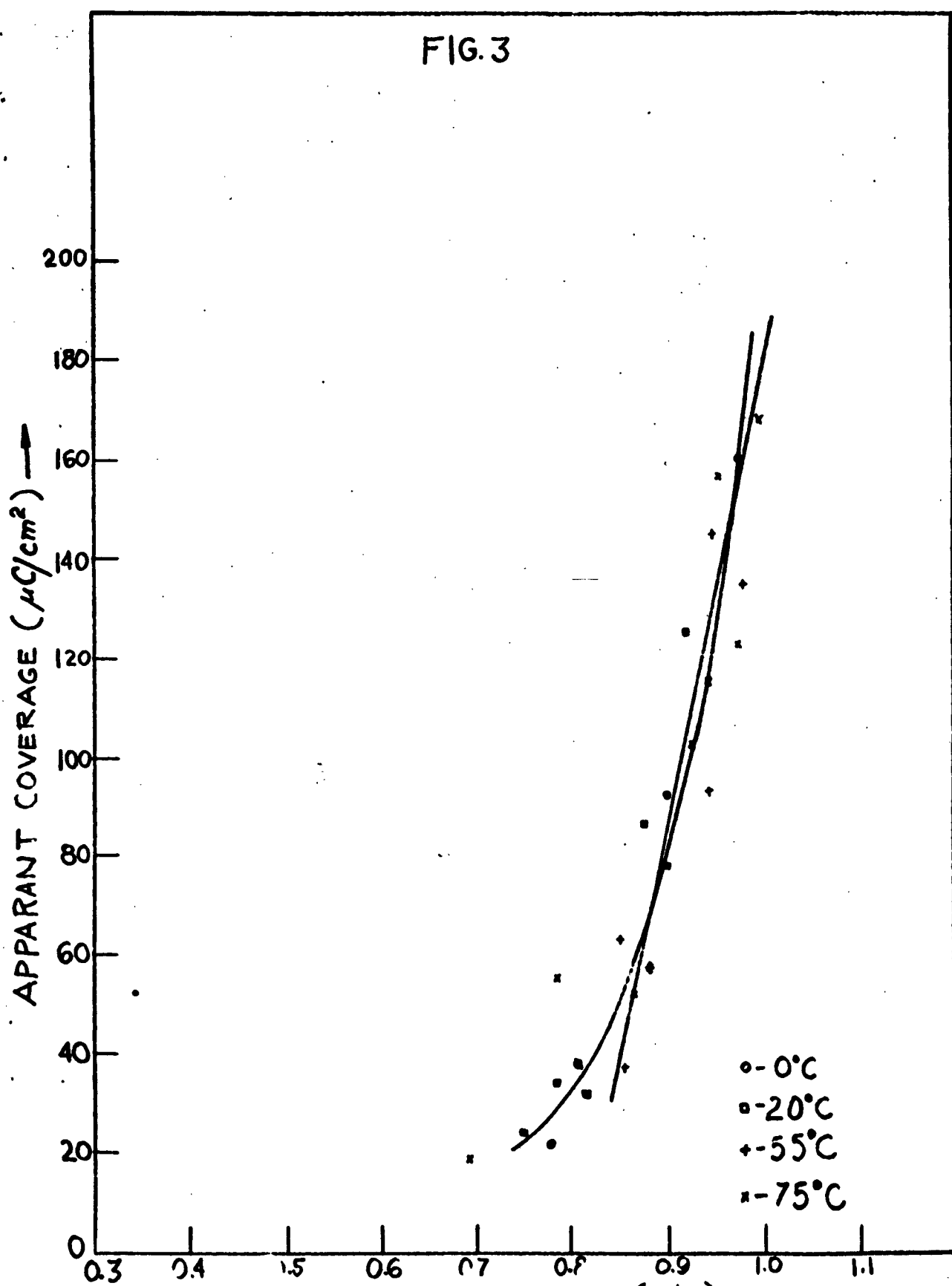


FIG. 4

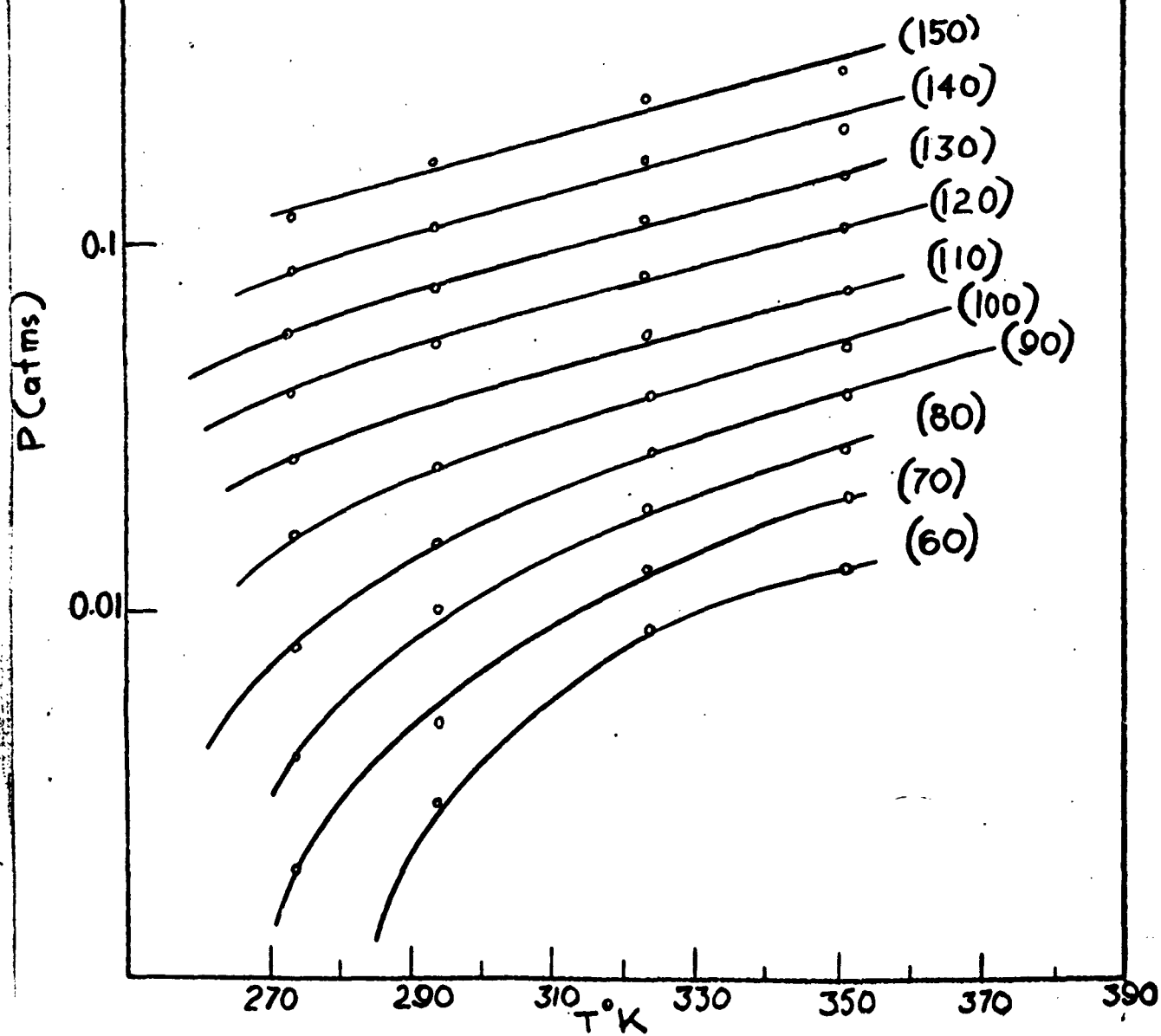


FIG 5

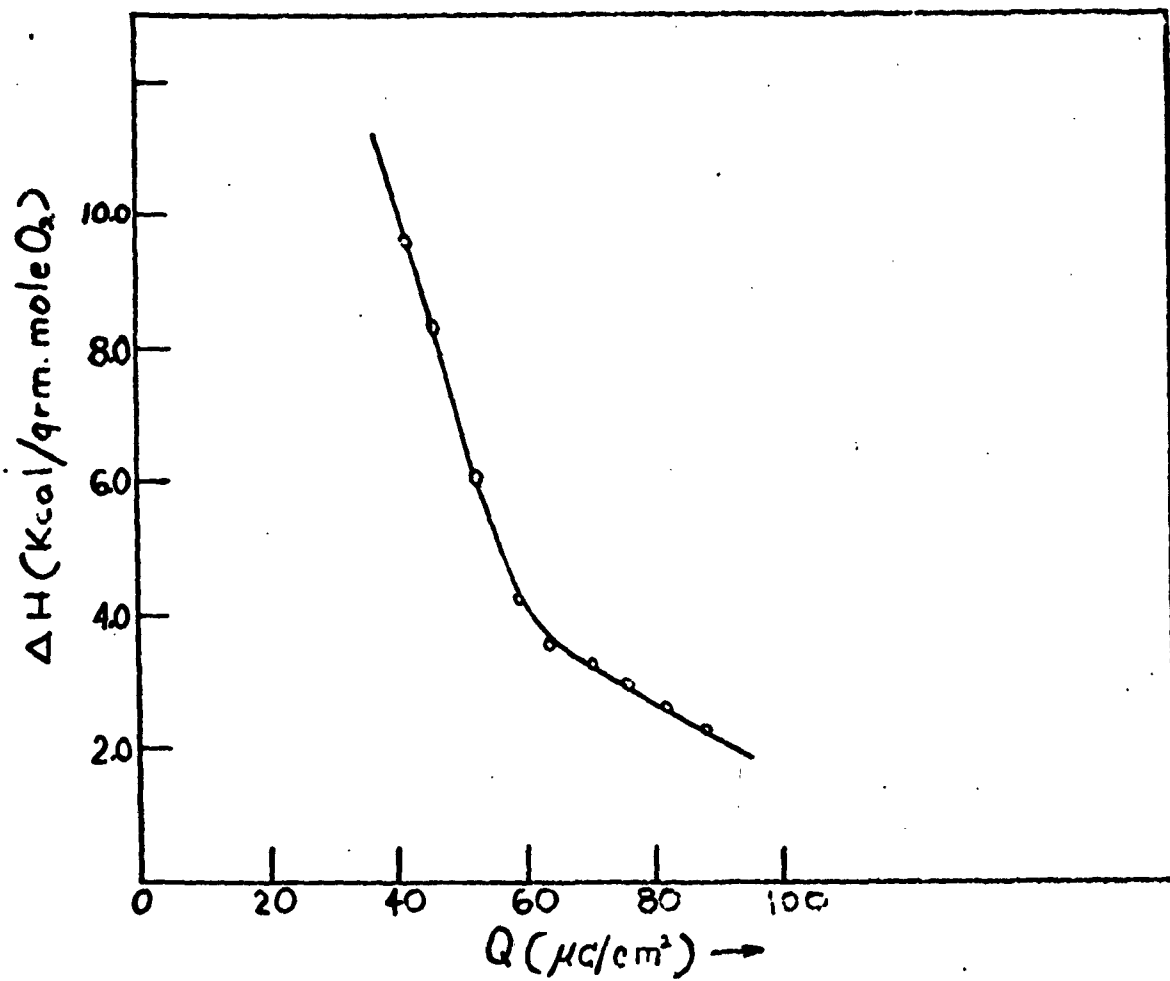
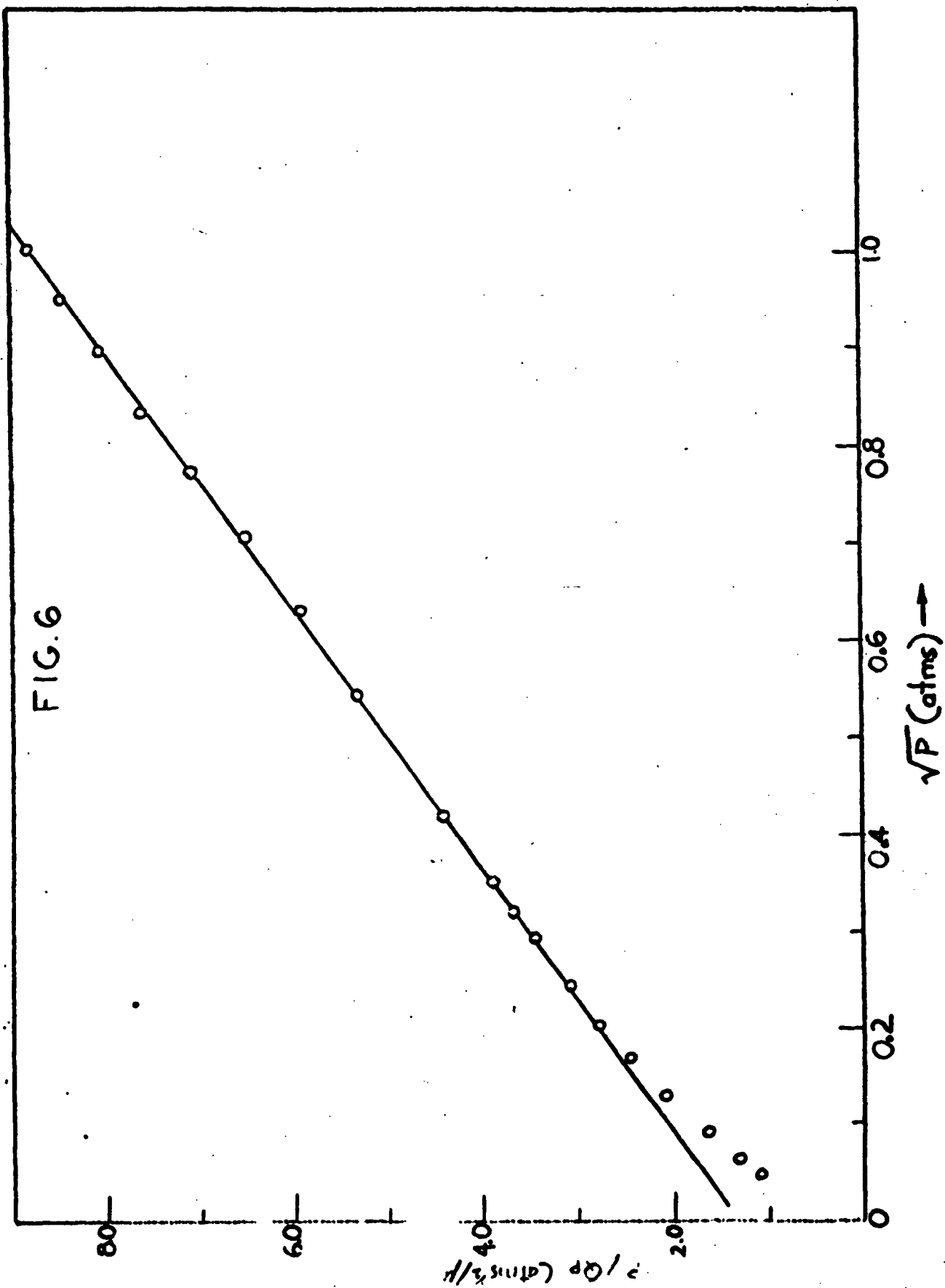


FIG. 6



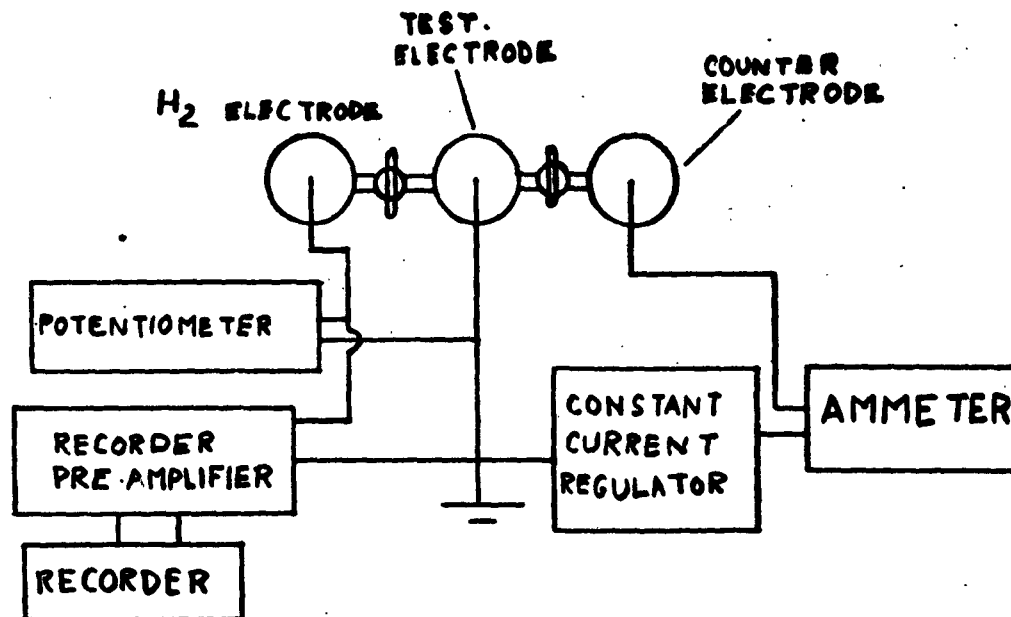


FIG. 7

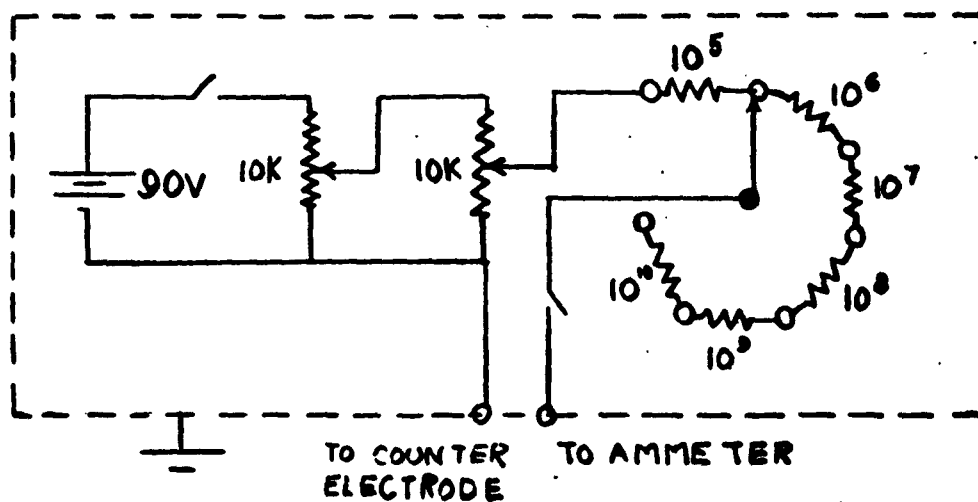


FIG. 8

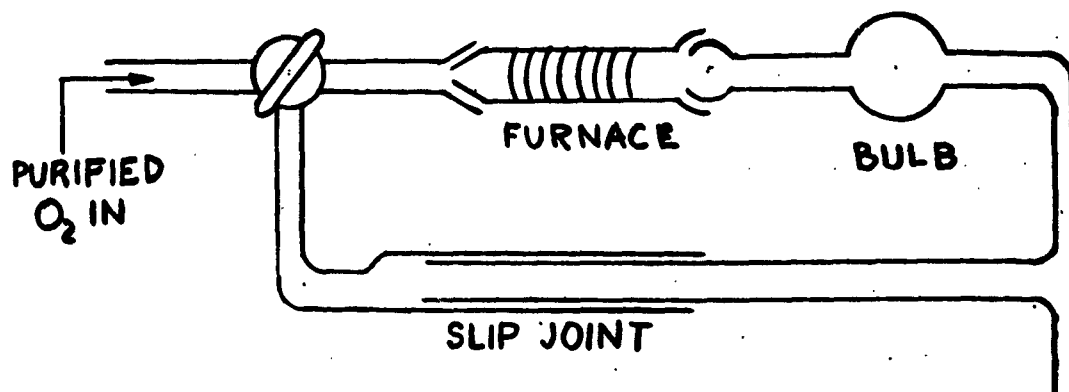
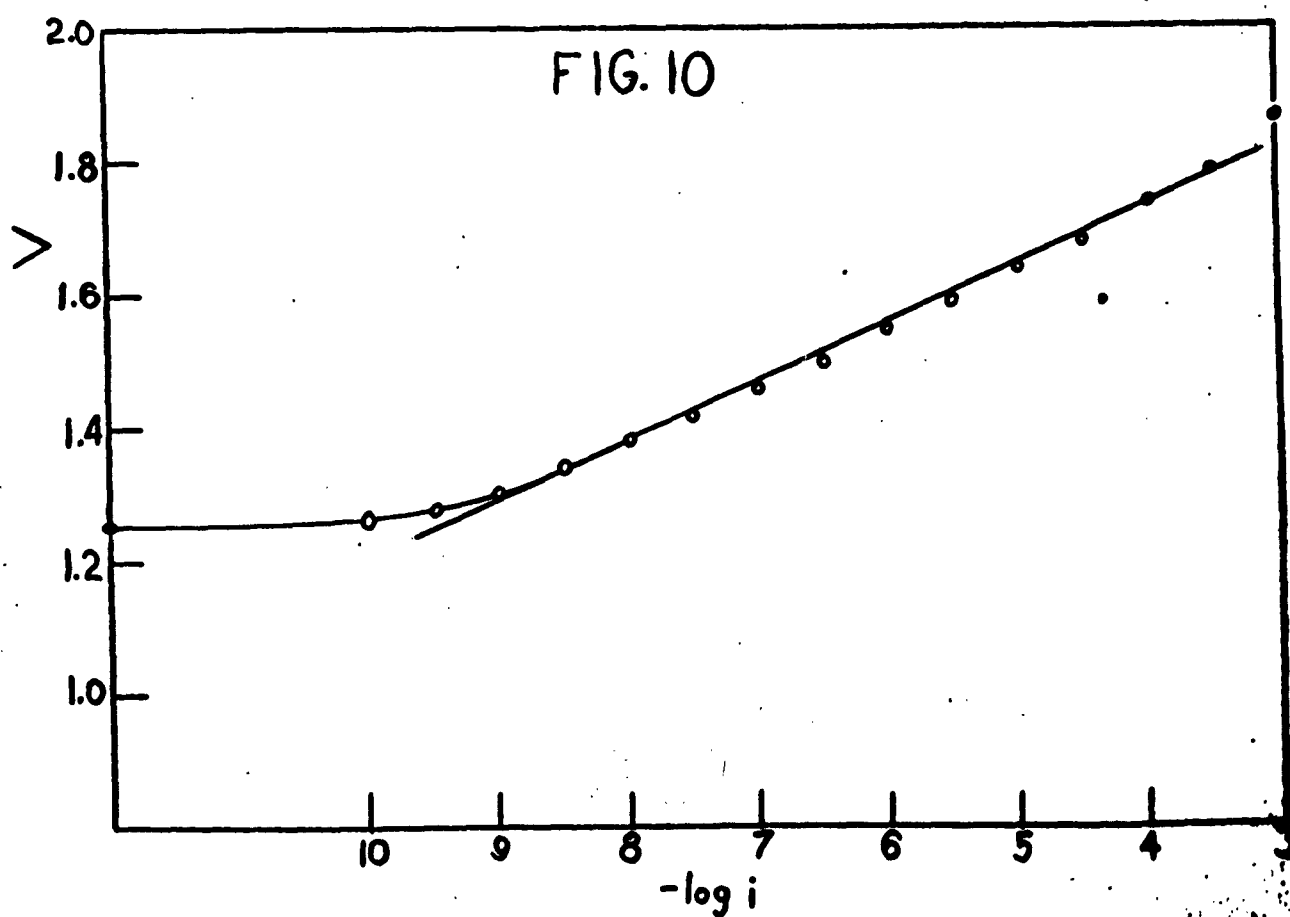


FIG. 9



<p>AD No. Accession No. University of Pennsylvania, Electrochemistry Laboratory Philadelphia 4, Pennsylvania REVERSIBLE OXYGEN ELECTRODES, by A. Dulacourio, M. L. B. Rao, and M. Gombosi; Unclassified Fourth Quarterly Report for the Period 1 August 1963 to 31 December 1963, 10 pp. Contract DA-36-039-SC-88921, Task No. 3499-09-001-02 Adsorption of oxygen on oxide free platinum electrodes in pure 1 N H₂SO₄ solutions saturated with oxygen at various partial pressures has been determined for 0, 20, 50, and 80%. Heat of adsorption has been evaluated for various coverages; it decreases with increasing coverage. At 0%, the heat of adsorption is 9,600 and 2,300 cal/mol O₂ for 40 O/cm² and 90 μO/cm², respective- ly. Plot of $\sqrt{\frac{Q}{Q_{\infty}}}$ versus \sqrt{P} indicates that adsorption is disassociative. Maximum value of the coverage is about 135 μO/cm², corresponding to one oxygen atom to four platinum atoms. Good Tafel lines have been obtained in oxygen evolution reaction. Zero current potential corresponds to re- versible oxygen potential, 1.23 V.</p>	<p>UNCLASSIFIED 1. Electrochemistry Reversible Oxygen Electrodes 2. Contract DA-36-039-SC-88921</p>	<p>AD No. Accession No. University of Pennsylvania, Electrochemistry Laboratory Philadelphia 4, Pennsylvania REVERSIBLE OXYGEN ELECTRODES, by A. Dulacourio, M. L. B. Rao, and M. Gombosi; Unclassified Fourth Quarterly Report for the Period 1 August 1963 to 31 December 1963, 10 pp. Contract DA-36-039-SC-88921, Task No. 3499-09-001-02 Adsorption of oxygen on oxide free platinum electrodes in pure 1 N H₂SO₄ solutions saturated with oxygen at various partial pressures has been determined for 0, 20, 50, and 80%. Heat of adsorption has been evaluated for various coverages; it decreases with increasing coverage. At 0%, the heat of adsorption is 9,600 and 2,300 cal/mol O₂ for 40 O/cm² and 90 μO/cm², respective- ly. Plot of $\sqrt{\frac{Q}{Q_{\infty}}}$ versus \sqrt{P} indicates that adsorption is disassociative. Maximum value of the coverage is about 135 μO/cm², corresponding to one oxygen atom to four platinum atoms. Good Tafel lines have been obtained in oxygen evolution reaction. Zero current potential corresponds to re- versible oxygen potential, 1.23 V.</p>	<p>UNCLASSIFIED 1. Electrochemistry Reversible Oxygen Electrodes 2. Contract DA-36-039-SC-88921</p>	<p>AD No. Accession No. University of Pennsylvania, Electrochemistry Laboratory Philadelphia 4, Pennsylvania REVERSIBLE OXYGEN ELECTRODES, by A. Dulacourio, M. L. B. Rao, and M. Gombosi; Unclassified Fourth Quarterly Report for the Period 1 August 1963 to 31 December 1963, 10 pp. Contract DA-36-039-SC-88921, Task No. 3499-09-001-02 Adsorption of oxygen on oxide free platinum electrodes in pure 1 N H₂SO₄ solutions saturated with oxygen at various partial pressures has been determined for 0, 20, 50, and 80%. Heat of adsorption has been evaluated for various coverages; it decreases with increasing coverage. At 0%, the heat of adsorption is 9,600 and 2,300 cal/mol O₂ for 40 O/cm² and 90 μO/cm², respective- ly. Plot of $\sqrt{\frac{Q}{Q_{\infty}}}$ versus \sqrt{P} indicates that adsorption is disassociative. Maximum value of the coverage is about 135 μO/cm², corresponding to one oxygen atom to four platinum atoms. Good Tafel lines have been obtained in oxygen evolution reaction. Zero current potential corresponds to re- versible oxygen potential, 1.23 V.</p>	<p>UNCLASSIFIED 1. Electrochemistry Reversible Oxygen Electrodes 2. Contract DA-36-039-SC-88921</p>
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